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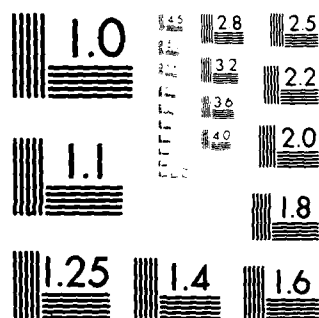
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TWO-DIMENSIONAL MASS SPECTROMETRIC  
SEPARATION AND IDENTIFICATION OF  
COMPLEX MIXTURES

FINAL REPORT

1 MARCH 79 - 29 FEBR. 82

F. W. McLAFFERTY

10 MAY 1982

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DEPARTMENT OF CHEMISTRY  
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Mass spectrometry; trace compound analysis; molecular structural determination; collisional activation mass spectra; unimolecular decompositions of gaseous organic ions.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The new technique of tandem mass spectrometry (MS/MS) has been investigated, in particular for the analysis of complex organic mixtures for trace components. Applicability, limitations, and improvements studied include those involving sensitivity, specificity, accuracy, speed, and identification of unknown components. The technique has been applied to important problems in targeted com- pound analysis, targeted class analysis, molecular structure deter-		

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mination, and unimolecular ion decomposition mechanisms. A unique tandem double-focusing mass spectrometer has been constructed, improved, and applied to these research problems.

#### Statement of the Problem

For complex mixture analysis, the need for methods of improved sensitivity, accuracy, specificity, and speed which are capable of continuous automatic monitoring is well known. Potential fields of application include many of critical importance, such as the detection of toxic substances, pollutants, and explosives, and the identification of adulterants or degradation products in foods, textiles, and construction materials. The potentialities of tandem mass spectrometry (MS/MS) for such problems have attracted a great deal of attention in the last few years, and there has been an explosive growth of unique applications as well as instrument capabilities and fundamental understanding of the underlying principles. MS/MS can be thought of as a two-dimensional "separator/identifier" system similar to the well-known combined techniques of gas and liquid chromatography/mass spectrometry (GC/MS and LC/MS). MS/MS is particularly advantageous for the analysis of specific organic compounds in complex mixtures. The targeted compound is selectively ionized, and its characteristic ions are separated from most others of the mixture in the first mass spectrometer (MS-I). The selected primary ions are then decomposed by collision, and from the resulting products the final mass analyzer (MS-II) determines secondary ions characteristic of the targeted compound. There was overlapping support of this research by NIH grant GM16609, under which there was special emphasis on MS/MS for analysis and structure elucidation of high molecular weight compounds of biomedical significance.

#### Summary of the Most Important Results

Construction of a unique tandem double-focusing instrument was completed, and this has recently been modified for high mass capabilities and improved reliability. This is still the only instrument of its kind in the world for such MS/MS research. Its high resolution capabilities for both MS-I and MS-II, the unusually high ion kinetic energies possible for collisionally activated decomposition (CAD), and the unusual efficiency of its unique molecular beam collision region, have been utilized in a variety of analytical and research applications. The 37 cm, 23 Kgauss MS-II magnet has a higher mass range than any commercial "single MS" (as well as MS/MS) instrument; the new 60 cm, 23 Kgauss MS-I magnet has four times the mass range of the very recent commercial "high mass" instruments, and 16 times the mass range of most others.

Publications resulting from this research have included several review articles publicizing the potentiality of the method, and a forthcoming book on "Tandem Mass Spectrometry." Applications have

included direct analysis for targeted compounds at trace levels and for targeted classes of compounds. A sampling technique for continuous liquid introduction, developed earlier in this laboratory as an LC/MS interface, has been investigated as a possible improved method for the ionization of nonvolatile compounds through submicro-second solution vaporization. Research on underlying principles includes the decomposition mechanisms of even electron ions, which can be a primary process in MS/MS in contrast to the situation in normal mass spectra; isotopic abundances in CAD mass spectra of ions containing polyisotopic elements; structural elucidation of more complex molecules; and basic chemistry of unimolecular ion decomposition processes.

An extensive investigation, as yet unpublished, has been made on instrumentation configurations which would give MS/MS with a two-dimensional real-time display of both the MS-I and MS-II results. A possible design incorporating tandem time-of-flight mass spectrometers has been proposed, and a variety of details of the design have been worked out. Further refinement and actual construction are proposed in the application for renewal of this grant.

#### Publications Resulting from this Research

Many of these publications also acknowledge financial support of the National Institutes of Health.

1. McLafferty, F. W. Unimolecular Decompositions of Even-Electron Ions", Org. Mass Spectrom. 1980, 15, 114-121.
2. McLafferty, F. W. Tandem Mass Spectrometry (MS/MS): A Promising New Analytical Technique for Specific Component Determination in Complex Mixtures, Acc. Chem. Res. 1980, 13, 33-39.
3. McLafferty, F. W.; Todd, P. J.; McGilvery, D. C.; Baldwin, M. A. High-Resolution Tandem Mass Spectrometry (MS/MS) of Increased Sensitivity and Mass Range, J. Am. Chem. Soc. 1980, 102, 3360-3363.
4. Lory, E. R.; McLafferty, F. W. Ionization of Nonvolatile Compounds by Submicrosecond Solution Vaporization, Adv. Mass Spectrom. 1980, 8, 954-960.
5. McLafferty, F. W.; Todd, P. J.; McGilvery, D. C.; Baldwin, M. A.; Bockhoff, F. M.; Wendel, G. J.; Wixom, M. R.; Niemi, T. E. MS/MS: A New Separation/Identification Technique for Complex Organic Mixtures, Adv. Mass Spectrom. 1980, 8, 1598-1596.
6. McLafferty, F. W.; Todd, P. J. An Alternative Configuration for Triple-Analyzer Mass Spectrometers, Org. Mass Spectrom. 1980, 15, 272.

7. Bowen, R. D.; Barbalas, M. P.; Pagano, F. P.; Todd, P. J.; McLafferty, F. W. Collisional Activation Spectra of  $[C_3H_6]^+$  Ions: The Structure of the Daughter Ion Produced by Methane Loss from Ionized Butane, Org. Mass Spectrom. 1980, 15, 51.
8. McLafferty, F. W.; Lory, E. R. Mass Spectrometry as a Separation Technique; the Analysis of Involatile Samples, J. Chromatog. 1981, 203, 109-116.
9. Todd, P. J.; Barbalas, M. P.; McLafferty, F. W. Collisional-Activation Mass Spectra of Ions Containing Polyisotopic Elements, Org. Mass Spectrom. 1981, 17, 79-80.
10. McLafferty, F. W. Tandem Mass Spectrometry (MS/MS) in Trace Toxicant Analysis, Biomed. Mass Spectrom. 1981, 8, 446-448.
11. McLafferty, F. W. Tandem Mass Spectrometry, Science 1981, 214, 280-287.
12. McLafferty, F. W. Mass Spectrometry in Complex Mixture Analysis in "Frontiers of Analytical Techniques and Their Application"; Philip Morris, Inc.: New York City, 1982.
13. McLafferty, F. W.; Barbalas, M. P.; Cheng, M. T.; Cohen, S. L.; Dhis, P. O.; Kruppa, G. H.; Proctor, C. J.; Turecek, F. Mass Spectrometry Combined with Mass Spectrometry, Adv. Mass. Spectrom. 1982, 9, to be published.
14. Cheng, M. T.; Kruppa, G. H.; McLafferty, F. W.; Cooper, D. A. Tandem Mass Spectrometry: Structural Information from China White and Related Fentanyl Derivatives, Anal. Chem., submitted.
15. Barbalas, M. P.; McLafferty, F. W. Methyltropylium Cation, The Most Stable  $[C_8H_9]^+$  Isomer, Org. Mass Spectrom., submitted.
16. Barbalas, M. P.; Turecek, F.; McLafferty, F. W. Hydrogen Chloride Elimination from Chloroalkane Molecular Ions, Org. Mass Spectrom., submitted.
17. Barbalas, M. P.; Turecek, F.; McLafferty, F. W. A Reinvestigation of the Stabilities of Isomeric  $[C_3H_6]^+$  Ions, J. Am. Chem. Soc., submitted.
18. McLafferty, F. W., ed. "Tandem Mass Spectrometry"; John Wiley: New York, 1982.
19. Staedeli, W.; Mun, I. K.; McLafferty, F. W. A Probability Based Matching System for Mass Spectra from Collisionally Activated Decompositions, Anal. Chem., submitted.
20. Turecek, F.; McLafferty, F. W. Approximate Energy Surface for  $[C_2H_3O]^+$  Ions Including an Additional Stable Isomer, Org. Mass Spectrom., submitted.

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21. Turecek, F.; McLafferty, F. W. Rearrangement and Methyl Loss from Molecular Ions of Propene Oxide and Methylvinyl Ether, Org. Mass Spectrom., submitted.

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